REMARKS

Claims 1, 3, 4, 8, 10, 12, 15-17 and 25-65 are pending in this application. Claims 1 and 46 have been amended to more particularly point out what Applicants regard as their invention. No new matter has been introduced.

The claimed invention is directed to, among other things, arrangements for generating hydrogen gas which include a check valve <u>in a gas conduit that connects product and fuel chambers</u>. A check valve is a mechanical valve that allows flow in a single direction and prevents backflow (see attached Exhibit A entitled "Tech Brief"). Such valves may be utilized in a compressor or other auxiliary apparatus. The claimed invention requires a check valve in a gas conduit line, but does not require a compressor. The check valve in the claimed invention prevents pressure equalization of the fuel and spent fuel chambers via the conduit line between them. Thus, any pressure buildup in the fuel chamber can only be released by pushing fuel through the catalyst chamber.

Claims 1, 25-29, 31, 32, 46, 47 and 49 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Amendola (U.S. Patent Appl. Pub. No. 2004/0033194) ("Amendola") in view of Carlson (U.S. Patent No. 3,951,568). Applicants respectfully traverse this rejection.

Reliance on Amendola as the basis for rejecting claims 1, 25-29, 31, 32, 46, 47 and 49 is not permitted to preclude patentability under 35 U.S.C. § 103(a), as provided by 35 U.S.C. § 103(c).

More specifically, the present application was filed on July 11, 2001. Amendola was filed on August 11, 2003 (with a priority date of January 7, 2000) and published on February 19, 2004. Amendola thus qualifies as prior art only under 35

U.S.C. § 102(e). In addition, the subject matter of Amendola and that of the claimed invention were, at the time the invention was made, subject to an obligation of assignment to the same entity: Millennium Cell, Inc. The Assignment for this application was recorded in the PTO on July 19, 2005, on Reel 016787, Frame 0363. The Assignment for Amendola is shown on the face of U.S. Patent 6,534,033, which issued based on the parent application of Amendola. Therefore, section 35 U.S.C. § 103(c) applies and the rejection is overcome and should be withdrawn.

Claims 1, 25-29, 31, 32, 46, 47 and 49 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Kojima (U.S. Patent Appl. Pub. No. 2001/0022960) in view of Nordskog (U.S. Patent No. 4,601,305). Applicants respectfully traverse this rejection.

Amended independent claim 1 recites an "arrangement for generating hydrogen gas" comprising "a catalyst chamber comprising a catalyst," "a fuel chamber connected to the catalyst chamber, the fuel chamber being configured to store a reactant material comprising a borohydride capable of generating hydrogen gas when contacting said catalyst" and "a spent fuel chamber . . . configured to receive borate and hydrogen gas, the borate and the hydrogen gas being generated by contacting the borohydride and the catalyst." Amended independent claim 1 also recites (emphasis added) "a gas conduit in direct communication with the spent fuel chamber and with the fuel chamber, the conduit including a check valve . . . configured to allow unidirectional flow of the hydrogen gas." Amended independent claim 1 further recites "a hydrogen gas outlet conduit connected to the gas conduit."

Independent claim 25 recites an "[a]pparatus for use in a system for generating hydrogen" comprising "a fuel container having an internal pressure," "a reactant material capable of generating hydrogen disposed within said fuel container, said fuel container having an outlet port which can be opened and closed, said internal

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pressure pushing said reactant material through said outlet port when it is open," and "a product container." Independent claim 25 also recites "a gas conduit between the product container and the fuel container," and "a check valve in communication with said gas conduit, the check valve being configured to allow the hydrogen to flow in one direction."

Amended independent claim 46 recites an "arrangement for generating hydrogen gas" comprising "a catalyst chamber comprising a catalyst," "a fuel chamber connected to the catalyst chamber, the fuel chamber being configured to retain a reactant material under a predetermined pressure, said reactant material capable of generating hydrogen gas when contacting said catalyst" and "a spent fuel chamber connected to the catalyst chamber for receiving product material and hydrogen gas generated by contacting the reactant material and the catalyst." Amended independent claim 46 also recites "a gas conduit between the spent fuel chamber and the fuel chamber, and "a check valve in communication with said gas conduit, the check valve being configured to allow the hydrogen to flow in one direction."

Kojima refers to an apparatus comprising a fuel storage tank (1) connected to a catalyst chamber (2) via a pipe (3). A pipe (7) carries product materials and unreacted reactant material from the catalyst chamber to a hydrogen separator (8). Separator (8) is connected to the fuel storage tank (1) via pipe (9) [0076]. A compressor (10) to supply an aqueous solution is connected to the pipe (9). As the Office Action acknowledges, Kojima does not disclose or suggest any valve, much less the presently claimed check valve, in the pipe (9) of Kojima.

Nordskog refers to a check valve that is "useful in air conditioning compressor units." (Abstract.) The valve of Nordskog is installed <u>within a compressor</u> (C3/L44), to provide increased gas flow rates through portions of the compressor.

According to the Office Action (at page 4),

> Kojima et al. also discloses wherein a compressor (10) is
> located within the conduit, but fails to disclose the specific
> nature of the compressor.
>
> Nordskog discloses a compressor with a check valve and
> teaches wherein it is advantageous to provide such an
> assembly in order to improve efficiency (col. 1, lines 29-38).
> It would have been obvious ... to provide the compressor of
> Kojima et al. with the check valve of Nordskog in order to
> gain the recognized efficiency advantages.

As the Office Action acknowledges, there is no check valve in pipe (9) of

Kojima and there is no disclosure of the nature or details of Kojima's compressor.

Clearly, the compressor of Kojima is not an air conditioning compressor as in

Nordskog.

Even assuming, for the sake of argument, that the compressor of Kojima can

include a check valve – which it does not – there is still no disclosure or suggestion that

any such valve should be included in pipe (9) of Kojima, or be configured to allow

unidirectional flow of hydrogen gas. Rather, the compressor of Kojima is merely

"connected to the pipe (9)" and functions to "stably supply[] the complex metal

hydride solution." [0074] Thus, even if the compressor of Kojima should include a

check valve somewhere <u>within</u> the mechanical structure of the compressor, there still is

no disclosure or suggestion of the presently claimed "<u>gas conduit</u> in direct

communication with the spent fuel chamber and with the fuel chamber, <u>the conduit</u>

<u>including a check valve</u>, the check valve being <u>configured</u> to allow <u>unidirectional flow</u>

<u>of hydrogen gas</u>," of independent claim 1, or the similar requirements of independent

claims 25 and 46. Any modification of Kojima with the check valve of Nordskog would

only result in a check valve <u>within</u> an auxiliary apparatus (aqueous solution

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compressor), and would be configured to regulate the flow of the aqueous solution which is provided by the compressor of Kojima. Taken as a whole, the combination of references does not disclose or suggest the claimed check valve in a gas conduit between fuel and spent fuel chambers, and which is configured to allow unidirectional flow of hydrogen gas between these chambers.

Furthermore, a person of ordinary skill in the art would not have been motivated to combine Kojima with Nordskog. Nordskog is directed to improving the efficiency of an air conditioning compressor. There is no disclosure or suggestion that a check valve would similarly be of any use in the compressor of Kojima, much less anywhere in the claimed systems which do not require any compressor.

For at least these reasons, the rejection of claims 1, 25-29, 31, 32, 46, 47 and 49 is overcome and its withdrawal is respectfully requested.

Claims 1, 25-29, 31, 32, 46, 47 and 49 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Falter (U.S. Patent No. 1,935,672) in view of Holmstrand (U.S. Patent No. 4,784,295). Applicants respectfully traverse this rejection.

Falter refers to an apparatus for continuously feeding a liquid material that is suitable for use in an arrangement for the conversion of acetylene to acetaldehyde and which comprises a chamber (2) containing a gaseous reactant material, a reaction kettle (1), a tank (7) for storing liquid reagents and catalyst (P1/89-92), "valved connections 3" to introduce acetylene into reaction kettle (1), product separation apparatus including condensers (23) and gas scrubbers (27) connected to both the reaction chamber (1) and a product collection receiver (25) (P1/L50-55), a spent liquor receiver (4) which receives spent material from the reaction chamber, and a conduit (28) for returning unconverted

reagent to the reagent chamber. However, neither the spent liquor receiver (4) of Falter nor the product collection receiver (25) is connected to the reagent chamber (2).

The Office Action at page 5 alleges that the "scrubbers" of Falter represent the presently claimed spent fuel chamber. In Falter, the scrubbers (27) remove gaseous product (e.g., acetaldehyde) from the unconverted reactant material (e.g., acetylene) by the counter-current flow of water though the gases: "...gases are...<u>passed through</u> a series of scrubbers 26 and 27..., the liquid from the scrubbers likewise emptying into the receiver 25." (Falter at P2/L52-77). In effect, the water is "washing" the gas. As known in the art, a scrubber is a column configured for flow-through operation (see the figures in the attached Exhibit B, entitled "Scrubbing Pollutants from Vent Streams," and Exhibit C, entitled "Flue-Gas Desulfurization 'Scrubbers'"). The product is then collected in product collection receiver (25) connected to the scrubbers and condensers via conduit 24 (P2/L52-78). Conduit 28 returns recovered reactant material to chamber (2) (P2/L78-82), but does not connect product receiver (25) to the reactant chamber (2).

The scrubber (27) of Falter, however, is not the same either structurally or functionally as the "spent fuel chamber" of the claimed invention. A scrubber requires two fluid streams (and two sets of inlets and outlets) to flow counter-current to each other through the device. In addition, scrubbers do not have any volume available to collect and store liquid or solid product material in the flow-through device. The spent fuel chamber of the claimed invention is not configured for counter-current flow and has at a minimum one inlet (i.e., the connection to the catalyst chamber) and one outlet (i.e., the gas conduit); a drain can be incorporated into the tank to remove collected material as desired. In contrast to a scrubber, the chamber collects and holds at least some of the product material ("spent fuel collected in chamber 30" [0028]).

Holmstrand does not disclose or suggest any of these missing elements of

Falter. The Office Action's rejection of claims 1, 25-29, 31, 32, 46, 47 and 49 should be

withdrawn for at least this reason.

In addition, the Office Action goes on to assert (at page 5, emphasis added):

> Falter discloses ... <u>a gas outlet</u> (29) connected to the gas
> conduit (28).
>
> Falter fails to disclose wherein it is well known to provide a
> vent with a check valve.
>
> Holmstrand discloses wherein it is well known <u>to provide a</u>
> <u>vent with a check valve</u> and teaches wherein it is
> advantageous to provide such in order to control the flow
> through the vent (col. 3, lines 47-50). It would have been
> obvious ... to provide the gas outlet (29) of Falter with a
> check valve as taught by Holmstrand in order to gain the
> recognized flow control.

As the Office Action acknowledges, Holmstrand only refers to a check valve

which can be incorporated into a vent: "vent conduit 36 which vents intermediate

chamber" (C3/L47-50). This valve serves to seal the system from the atmosphere via the

vent conduit so that "all air employed to purge the system must be admitted through

nozzle 14" (C3/L50-53).

In direct contrast, the claimed invention requires a check valve <u>in the gas</u>

<u>conduit</u> that connects the product and fuel chambers, and not in the separate outlet

conduit (see, for example, specification paragraph [0023]: "...a conduit [unnumbered

element in Figure 1, and shown containing valve 40] having a check valve 40 which

allows hydrogen gas flow only in one direction. A hydrogen gas conduit line 50

conveys hydrogen gas out of the system"). Any combination of Falter and Holmstrand

would only result in a check valve in the outlet vent of Falter, and not in any conduit between fuel and product chambers.

For at least this additional reason, the combination of Falter and Holmstrand fails to disclose, teach or suggest a fuel chamber and product chamber connected by a gas conduit including a check valve, as in the claimed invention.

Furthermore, one of ordinary skill would have found absolutely no motivation to modify Falter with a check valve according to Holmstrand, because Holmstrand specifically states that "in practice, it has been <u>found more advantageous to omit [check] valve 44</u> and constantly vent chamber 32 to the atmosphere" (C3/L56-58; emphasis added). One of ordinary skill reading Holmstrand would find no motivation to modify Falter by using a check valve and, even if this combination was proper – and it is not –the combined cited references would result in, at most, a check valve in Falter's vent, i.e., gas outlet (29), which is clearly distinct from the claimed invention.

Accordingly, the § 103 rejection over Falter and Holmstrand is overcome for at least the foregoing reasons and should be withdrawn.

With respect to the provisional rejection of claims 25-29, 31, 32, 46, 47 and 49 under the judicially-created doctrine of obviousness-type double patenting as being unpatentable over claims 1-34 of co-pending Application Serial No. 09/900,625, filed on July 6, 2001; over claims 1-13 of co-pending Application Serial No. 10/638,651, filed on August 11, 2003; over claims 1-18 of co-pending Application Serial No. 10/223,871, filed on August 20, 2002; over claims 1-28 of co-pending Application Serial No. 10/359,104, filed on February 5, 2003; and over claims 1-45 of co-pending Application Serial No. 10/115,269, filed on April 2, 2002, Applicants resubmit that these rejections are

provisional and that Applicants will respond to these rejections upon the indication of

allowable subject matter.

The pending claims are believed to be in condition for immediate allowance.

If anything further may be required to place these claims in even better form for

allowance, the Examiner is cordially invited to telephone the undersigned attorneys for

Applicants.

Dated: August 10, 2006   Respectfully submitted,

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EXHIBIT A

Tech Brief

Valves

by **Z. Michael Lahlou**, Ph.D., Technical Assistance Consultant

Summary

Valves direct, start, stop, mix, or regulate the flow, pressure, or temperature of a fluid. Valves range from simple water faucets to control valves equipped with microprocessors. Many different valve types exist; however, the most common types include gate, plug, ball, butterfly, check, pressure relief, and globe valves.

What are the valve functions?

Valve functions vary based on the position of the closure element in the valve. The closure position can be adjusted manually or automatically. Valves usually fall into one of three classes:

1. shut-off valves block the flow or allow it to pass;
2. anti-reversal valves allow flow to travel in one direction; and
3. throttling valves regulate flow at a point between fully open to fully closed.

However, specific valve-body designs may fit into one, two, or all three classifications.

What are the basic valves?

Manual Valves *(See Figure 1)*

Manual valves require manual operation, such as a hand wheel or lever, which are primarily used to stop and start flow (shut-off valves), although some designs can be used for basic throttling. A manual valve operator is any device that requires the presence of a human being to operate the valve, as well as to determine the proper action (open, closed, or a throttling position). Manual valves are also used to divert or combine flow through a three- or four-way design configuration. Four types of manual valves exist:

1. rotating valves, such as plug, ball, and butterfly valves;
2. stopper valves, such as globe and piston valves;
3. sliding valves, such as gate and piston valves; and
4. flexible valves, such as pinch and diaphragm valves.


Figure 1 - Manual Valves

Ball Valve — Butterfly Valve — Diaphragm Valve — Gate Valve — Pinch Valve — Globe Valve
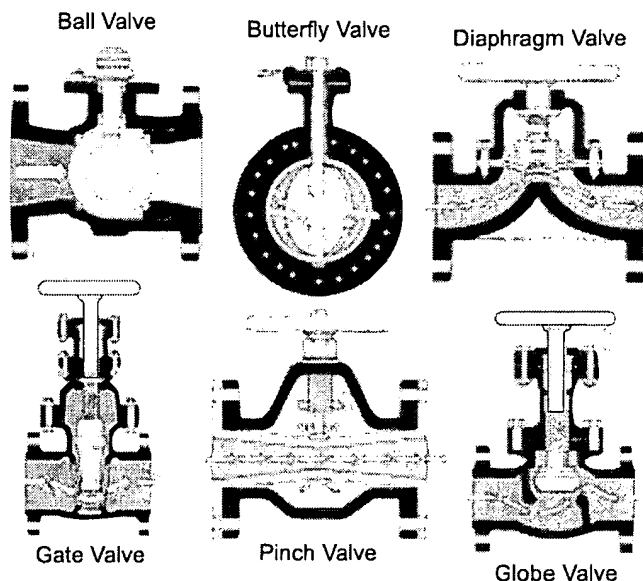
Check Valves *(See Figure 2)*

Check valves are automatic valves that open with forward flow and close against reverse flow. Check valves, also known as non-return valves, prevent return or reverse flow and maintain pressure. Check valves do not require an outside power supply or a signal to operate. In fact, a check valve's operation depends upon the direction in which the water is flowing. A pump or a pressure drop may determine water flow. If the flow stops or if pressure conditions change so that flow begins to move backward, the check valve's closure element moves with the reverse flow until it is seated, preventing any backward flow. There are different types of check valves, but they all have the same

PAGE **one** OF FOUR

Figure 2 - Check Valves

Check Valve
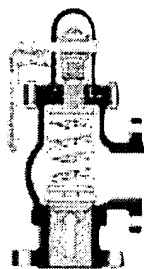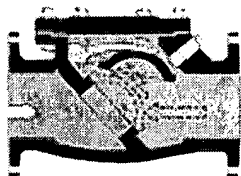
Relief Valve

operating principle. Check valves include lift-check valves, swing-check valves, tilting-disk valves, split-disk valves, and diaphragm-check valves.

Pressure Relief Valves

A pressure-relief valve is used to protect against over-pressurization of the system. When excess line pressure is detected, the pressure-relief valve automatically opens and relieves the excess pressure. A pressure-relief valve is installed where excess pressure constitutes safety concerns, such as pipes or equipment bursting. Following the depressurization of the water line to safe or normal limits, the pressure-relief valve automatically closes again to allow for normal system operation.

Control Valves *(See Figure 3)*

Control valves, also known as automatic control valves, are used to regulate flow anywhere from fully open to fully closed. Control valves are a fast growing segment of the valve industry because of the quickening pace of water-industry automation. Control valves are almost always equipped with some sort of actuator or actuation system (See definition under Manual Operators and Actuators below.) Manually operated valves and pressure regulators can stand alone in a throttling application, while a control valve cannot. Hence the difference: a control valve is a throttling valve, but not all throttling valves are control valves.

Manual Operators and Actuators

With most valves, some mechanical device or external system must be devised to open or close the valve or to change the position of the valve. Manual operators, actuators, and

actuation systems are those mechanisms that are installed on valves to allow this action to take place. Automatic valve control requires an actuator, which is defined as any device mounted on a valve that, in a response to a signal, automatically moves the valve to the required position using an outside power source.

What are common valve problems?

Pressure drop or pressure differential, which is the difference between the upstream and downstream pressures, makes water flow move through a valve. If the piping size is identical both upstream and downstream from the valve and the velocity is consistent, the valve will use frictional losses to reduce the fluid pressure and create flow. Because the pressure drop that a valve generates absorbs energy through frictional losses, an ideal pressure drop allows the full flow to pass through the valve's body without excessive velocity, absorbing less energy.

However, some systems may need to take a larger pressure drop through the valve. A high-pressure drop through a valve creates a number of problems, such as cavitation, flashing, choked flow, high noise levels, and vibration. Such problems present a number of immediate consequences: erosion or cavitation damage to the body and trim, malfunction or poor performance of the valve itself, attached instruments will not remain calibrated, piping fatigue, or hearing damage to nearby workers. In these instances, valves in high-pressure-drop applications require expensive trims, more frequent maintenance, large spare-part inventories, and piping supports. Such measures drive up maintenance and engineering costs.

Figure 3 - Control Valves

Control Valve

Although users typically concentrate on the immediate consequences of high-pressure drops, the greatest threat a high-pressure drop presents is lost system efficiency. Usually, a pump adds pressure and, thus, energy to the system. As the system absorbs more energy, including the energy that valves with high-pressure drops lose, it must use larger pumps. Consequently, if the system is designed with few valves
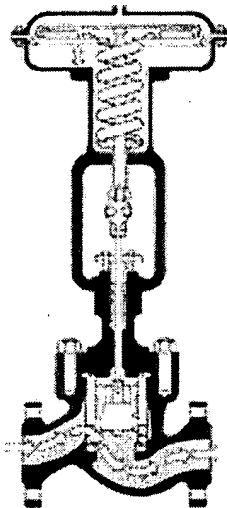
with high-pressure drops, the system is more efficient and able to use smaller pumps.

Cavitation
Cavitation happens when low-pressure bubbles suddenly form and then collapse within a small area of the valve within microseconds. Minor cavitation damage may be considered normal for some applications, which can be dealt with during routine maintenance. If unnoticed or unattended, severe cavitation damage can limit the life expectancy of the valve. It can also create excessive leakage, distort flow characteristics, or cause the eventual failure of the valve body and piping. In some severe high-pressure drop applications, cavitation can destroy valve parts within minutes.

One of three basic actions can control or eliminate cavitation. Operators can:
- modify the system;
- make certain internal body parts out of hard or hardened materials; or
- install special devices in the valve that are designed to keep cavitation away from valve surfaces or prevent the formation of the cavitation itself.

Flashing
When the downstream pressure is equal to or less than the vapor pressure, the vapor bubbles generated stay intact and do not collapse. This phenomenon is known as flashing. When flashing occurs, the fluid downstream is a mixture of vapor and liquid moving at a very high velocity, which results in erosion in the valve and in the downstream piping.

Unfortunately, eliminating flashing completely involves modifying the system itself, in particular the downstream pressure or the vapor pressure. However, not all systems are easily modified and this may not be an option. When flashing occurs, no solution can be designed into the valve, except possibly using hardened trim materials.

Choked Flow
The presence of vapor bubbles that cavitation or flashing cause significantly increase the specific volume of the fluid. This increase rises at a faster rate than the increase that the pressure differential generates. If upstream pressure remains constant, decreasing the downstream pressure will not increase the flow rate. Choked flow must be considered when sizing a valve.

High Velocities
Large pressure differentials create high velocities through a valve and in downstream piping. This in return creates turbulence and vibration if the velocities are not lowered. Lower velocities will reduce problems associated with flashing and erosion.

Water Hammer Effects
A valve that is opened too quickly or slammed shut when the closure element is suddenly sucked into the seat ("bathtub stopper effect") as the valve nears shutoff may cause water-hammer effect. Although water hammer generates considerable noise, the real damage occurs through mechanical failure. Water hammer can burst or damage piping supports and connections. In valves, water hammer can create severe shock through trim, gasket, or packing failure.

With valves, the best defense against water hammer is to prevent any sudden pressure changes to the system. For example, one solution may involve slowing the closure of the valve itself. Adding some type of surge protection to the piping system can also reduce water hammer.

What are the operation and maintenance requirements?
To avoid mechanical failure, design a practical valve maintenance program, which can result in cost savings for the water system. A job that appears to be mammoth becomes less daunting if the operator implements a systematic maintenance schedule. Operation and maintenance procedures for various types of valves are included in the manufacturer's operation manuals and in the appropriate product standards. Valve records are essential for planning, operating, and verifying the system's integrity. The valve record should contain information about valve condition, testing, and maintenance required.

What about safety/terrorism?
Recent events have understandably heightened concern that water supplies may be vulnerable to terrorist attacks—biological, chemical, and structural. Relief from this concern can come via knowledge, planning, and preparedness. It is crucial now to regularly inspect the location, accessibility, and operation of all the valves in the distribution system. This inspection will reveal the condition of the valve box and chamber.

It also is imperative to update the location of the valves on the map. E. H. Wachs Companies for example, offer "Valvecard" software that allows water utilities to manage their valve distribution system from a desktop computer. The software can be used to create valve inventory databases that require a secure user-friendly system to input, store, and analyze valve data or to collect valve information directly from each valve in a system. The software also can be used to operate and exercise valves in the system and record this information or monitor the system and keep it operational at all times. It can perform queries regarding valve properties, location, activities, and conditions as well as interface with Geographic Information Systems and map files.

After having complete and accurate information about all the valves in the system, the utility manager can run through a large number of "what if" scenarios to determine where a contaminant is likely to move and how valves or other utility operations can control its movement. To do this, the utility needs a calibrated, extended-period simulation model. There are a few types of software on the market for water distribution modeling and engineering that allow system managers to view scenarios graphically. Some of this software, such as WaterCad by Haestad Methods, can give a clear picture of what is occurring or will occur in the system in response to any operational measures that management proposes.

U.S. Environmental Protection Agency and the American Water Works Association in collaboration with Sandia National Laboratories continue to develop a risk- and consequence-based vulnerability assessment technique to improve the safety and security of water supply and distribution systems against emerging physical, chemical, and biological threats.

Where can I find more information?
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Z. Michael Lahlou holds a doctorate in environmental and natural resource economics, a masters in civil and environmental engineering, and an MBA. Formerly the technical assistance coordinator for the National Drinking Water Clearinghouse, Lahlou now resides in Huntington Beach, CA.

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EXHIBIT B

Waste Gas Scrubbing.

Jaeger Products, Inc.
Houston, Texas

Gaseous emissions containing inorganic as well as organic pollutants are highly regulated and becoming more so in light of the Clean Air Act. Emission control of gas streams in an industrial setting can include very large applications associated with power generation as well as small vent and emergency release scrubbers. Packed column technology is well proven in most gas scrubbing applications, and is the technology of choice in the majority of applications due to low initial and operating cost, high efficiency, and reliability.

WHY USE SCRUBBING?

Scrubbing is a common name given the unit operation normally known as gas absorption. In this process, mass is transferred from the gas phase into a liquid for the purposes of removing material from the gas stream. Obviously, the material to be transferred has to be soluble in the liquid for the process to be effective and herein lies one of the most important aspects of scrubbing: selection of the proper scrubbing liquid.

In most air pollution control applications, the materials to be removed are usually acidic or basic gases even though in some cases, organic vapors are also present. Most of the inorganic contaminants are sulphur, phosphorous, halogen, or nitrogen oxides or acids. In other cases, ammonia or chlorine are of concern.

Wet scrubbers can achieve extremely high contaminant removals and can operate at a variety of loads. Operation and control are simple, very stable, and ideal for remote, unattended locations. Scrubbing can achieve simultaneous removal of various contaminants as well as provide a measure of gas cooling and particle emission control. With the correct configuration, a scrubber can be used to remove acids and alkalies, or even soluble organic compounds. Scrubbing produces a liquid waste stream in many cases that has to be dealt with, but in the majority of the cases, this liquid stream does not require post-treatment beyond neutralization.

WHAT IS SCRUBBING?

A waste gas stream is put in contact with a scrubbing liquid in a contactor, most commonly a packed column. The scrubbing liquid exhibits high solubility for the contaminants in the gas and these migrate from the gas into the liquid. In many instances, the liquid contains a reactive solute that enhances the degree of absorption by reacting with the contaminant once it dissolves and effectively removing it chemically. This chemical absorption process allows for effective scrubbing of fairly insoluble gases, such as SO_2, chlorine, and H_2S.

The scrubbing process takes place in a packed column where the packing provides the necessary surface area and turbulence to achieve the desired removal. The scrubbing liquid is distributed at the top of the packed bed and it "rains" down flowing through the bed where it comes in intimate contact with the gas. This contact allows the scrubbing liquid to remove a contaminant from the dirty gas.

Important variables in the design of a packed scrubber include the following:

--types and amounts of contaminants to be removed
--gas flow, temperature, molecular weight, and humidity
--type and composition of scrubbing liquid
--amount of dust present
--available or allowable pressure drop for system
--effluent limitations in terms of composition, temperature, entrained liquid
--means for disposal of purge scrubbing liquid

PACKED SCRUBBERS VS. OTHER TYPES

Many different types of scrubbers are used in industry. Spray, venturi and jet scrubbers are generally used when large amounts of solids are present and when heat transfer is required in quenching applications Packed scrubbers are indicated when high efficiency is required and when flexibility is desirable.

The main advantages packed scrubbers have over others are:

a) Packed scrubbers are more economical and effective for larger flows.

b) Packed scrubbers are more economical when large fractional removals are required (in excess of 98%).

c) Packed scrubbers operate at a fraction of the pressure drop of trayed ones. This reduces the horsepower requirements for air movement in the tower.

d) Packed scrubbers are more economical when high volatility compounds are to be removed because they offer very large transfer areas and the ability to operate counter-currently.

e) Packed scrubbers offer better turndown and operability range than any other type of scrubber.

WHAT DOES A TYPICAL PACKED GAS SCRUBBER UNIT LOOK LIKE?

The configuration of a scrubbing unit can vary depending on the characteristics of the material to be removed from the gas stream . Figure 1 depicts a countercurrent waste gas scrubber that can handle ammonia and acid gases in the same piece of equipment. This configuration would be typical of power generation applications and of cases where combustion gases need to be cleaned. Two separate cycles are present; the bottom section of the scrubber utilizes acidic water to remove ammonia and some of the more soluble acids. Ammonia is highly soluble in water at low pH values, so the acid loop absorption can be very effective. On the other hand, the acid components of the stream, including SO_2, are fairly insoluble in pure or acidic water but very soluble in caustic solutions at high pH values, thus the use of a caustic absorption loop.

The caustic solution is routinely a solution of sodium hydroxide (NaOH) in water and the by-products of absorption are a variety of soluble sodium salts. More flow is normally needed in the tower itself to provide good contact than the replacement flow required for make-up of spent caustic. The most economical arrangement involves a recycle loop for the scrubbing liquid with small make-up and purge streams.

The acidic water solution loop operates in a similar manner except that the low pH value is achieved by the absorption of acids from the feed gas. The purge from this cycle will be a sour water concentrated in ammonia. Suitable disposal or treatment needs to be available for this stream.

Other gas scrubbing applications involve only the acid gas absorption step. These applications can be found routinely in the pulp and paper industry where removal of HCL, chlorine, and chlorine oxides is needed from vent streams. Sodium hydroxide or sodium carbonate solutions are frequently employed as the scrubbing liquid.

Odor control applications involve scrubbing H_2S out of air. This is essentially an acid gas absorption application that uses a caustic scrubbing liquid. Vent stream from diverse manufacturing operations, such a anodizing, plating, or other metals treatment often have acid gases present that can be easily removed in a scrubber.

A very important application of scrubbing is the treatment of vent gases from process vessels and tanks. These vents can sometimes be continuous and part of routine operations or they can be emergency releases from safety devices. In any case, these vent streams are likely to contain a large number of contaminants to be removed, ranging from acid gases to organic vapors. It is not unusual to have separate scrubbers for inorganics and organics depending largely on water disposal constraints.

Finally, in many cases it is necessary remove moisture from process gases. This can be accomplished by absorbing or scrubbing water out of the gas stream using a hygroscopic solvent. Solvents can be liquids, such as sulfuric acid, glycols, or other heavy, hygroscopic compounds.

CROSS-FLOW SCRUBBERS

In many cases, and especially when a chemical reaction in the liquid phase is involved in the scrubbing process, cross-flow scrubbers are used. These devices operate in a similar manner to the traditional countercurrent devices with the exception that the gas flows horizontally in the packed bed. The liquid is still fed at the top and flows downward through the packing, but the contact between the liquid and the gas takes place in a cross-flow arrangement. Cross-flow scrubbers can be very effective especially when using a caustic solution to scrub an acid gas. They exhibit lower pressure drops and slightly higher capacities and have a horizontal profile that can be desirable when space restrictions exist. In general though, countercurrent scrubbers are capable of higher removal efficiencies and are able to minimize the amount of scrubbing liquid needed.

Jaeger Products, Inc. can assist you in the selection of the most economical flow arrangement for your scrubber given the constraints of your site and required performance.

Independently of the objective of the scrubber, the necessary hardware to be installed in the tower is similar regardless of scrubbing application. Figure 1 shows the packing and internals normally associated with a wet countercurrent scrubber. Various materials are available on all packings and internals to accommodate hot, corrosive, erosive, and dusty services.

DOES RECYCLE OF THE LIQUID HELP?

Many scrubbers operate with a recycle liquid stream from the bottom to the top. This is done when the material to be scrubbed reacts quickly in the liquid phase so that the actual concentration of the pollutant in the liquid is always very low. Recycle allows the scrubber to operate at reasonable wetting rates without the need for excessive make-up or purge of liquid. This arrangement is typical of ammonia and acid gas scrubbers.

Recycle, on the other hand, cannot be used when the pollutant does not undergo reaction in the liquid phase, such as scrubbing organic compounds into water or a solvent. In this case, once-through operation of the liquid is indicated to prevent accumulation of the pollutant in the liquid inlet.

CHEMISTRY, CHEMISTRY, CHEMISTRY!!

Scrubbers that remove reactive pollutants, such as ammonia and acid gases, depend heavily on the proper chemistry in the liquid phase for their effectiveness. It is of crucial importance that the designers and operators of scrubbers understand the chemistry of the system since more scrubbers fail because of faulty chemistry than any other reason.

This is of particular importance in systems that include a multitude of pollutants, since interaction among them can be serious. An excellent example is the typical mixed vent from a microelectronics manufacturing facility that includes HCL and ammonia. These two compounds react in the gas phase to make ammonium chloride, a white microscopic powder that is extremely difficult to remove and results in pervasive white plumes.

Jaeger Products has more experience than any other mass transfer supplier in tackling tough scrubbing problems from the chemistry to the equipment.

SOME PITFALLS IN SCRUBBING SYSTEM DESIGN.

Several aspects of the design of scrubbing systems are very crucial and not immediately obvious. First, is the accuracy and reliability of equilibrium and chemical reaction data. The thermodynamic model of choice for scrubbing systems is one based on activity coefficients that can predict solubilities as a function of temperature and composition. Two models that fit this function very well are the Wilson and Van Laar activity coefficient models. Interaction parameters for these models are readily available for most of the common contaminants.

Waste gases can be very fouling, especially when heavily laden with ash and inorganic salts. In typical scrubbing configurations, most of the fouling will occur in the bottom of the scrubber and design provisions are needed to allow for frequent cleaning. In many cases, especially when significant gas cooling is needed, it is recommended that a quench tower be used ahead of the scrubber to take the brunt of the fouling and cool the gases down. Cooler gases can be handled in a scrubber using less expensive materials of construction, if adequate control logic protection is provided to prevent damage to the scrubber if the quench were to fail. The quench tower can be packed or equipped with trays.

Design at low scrubbing solution make-up rates is desirable since it reduces the downstream processing requirements. Nevertheless, care must be taken to assure that the scrubbing power of the solution is not

diminished. Common practice limits the amount of absorption to a maximum of 25% of saturation (be it by

chemical reaction in the case of reactive absorption, or solubility when no reaction takes place) in the recycle loop. Some operations run at total recycle for a period of time and then replace the solution charge when it reaches 25% saturation. Others have a continuous make-up and purge.

Mass transfer will also occur from the liquid to the gas if conditions are favorable. Care must be exercised to account for any evaporative losses of the scrubbing liquid to the gas stream. This is especially important when non-aqueous scrubbing liquids are utilized.

Most absorption processes are exothermic since the materials removed exhibit significant heats of solution and/or reaction with the scrubbing liquid. A good example of this is the large heat release encountered in hydrochloric acid absorption. The design of the system, the selection of the liquid rate, and the selection of the materials of construction should take into account the temperature rise of the liquid caused by these heat effects.

THE SCRUBBER AND OTHER COLUMNS IN THE SYSTEM.

The contacting devices in the scrubbing system are where the transfer of mass takes place. Commonly, they are vertical countercurrent vessels filled with a mass transfer device. In general, these devices are either sieve trays, random packings, or structured packings (the level of efficiency and capacity follows the same order and so does their sensitivity to fouling). In some other cases, cross-flow arrangements can be had when height limitations are present.

The scrubbers are also equipped with liquid distributors and support plates for the packing. In the case of deep bed requirements, intermediate liquid collectors and redistributors are also installed to ensure good performance. Figure 2 shows different combinations of internals that can be installed in a scrubber. In most cases though only combinations of trays and packings (with the associated internals) are used. Jaeger Products, Inc. offers all internal devices necessary for scrubbers and quench columns in a variety of designs and materials to suit the application.

HOW CAN JAEGER HELP YOU IN SCRUBBING APPLICATIONS?

Jaeger Products, Inc. has extensive experience in the successful design of scrubbing systems for ammonia, acid gases, and organics removal. Our engineering staff can provide you with a complete process design, specify the contacting column in detail, and supply you with all process specification for the peripheral equipment as illustrated in Figure 1. Our data base is very extensive and chances are there are very few contaminants we have not tackled.

We have a complete line of packings, trays, and tower internals that can satisfy any scrubbing or absorption need. Since the performance of the system depends heavily on the correct internals selection, as well as on a good process design, Jaeger can assist you with both so that total responsibility is easily identified. Although we normally do not provide turn-key systems, we can direct and/or assist you in such a project. We can also put you in contact with a systems manufacturer that would provide a turn-key project with Jaeger engineering and hardware.

THE JAEGER ADVANTAGE

Typical Scrubbing Applications

SO_2 removal from stack gases
H_2S removal for odor and sulphur emission control
SO_3 removal from sulfuric acid plant vents
Removal of HCL, chlorine oxides, and chlorine
Alcohol, ketone, ether, and aldehyde removal from vent streams
Sulfuric and nitric acid emission control
Gas dehydration using hygroscopic solvents
Organics removal by use of heavy, large molecular weight solvents
CO_2 removal from gas streams
Vents from microelectronics manufacture
Vents from pulp and paper operations
Vents from rendering plants
Vents from chemical plants and refineries

Scrubbing facts

Capable of achieving very high removals and low gas effluent concentrations
Most economical removal technique at all gas feed concentrations
Cost effective at very low feed concentrations (ppm level)
Minimizes air emissions
Reduces loads to incineration
Can be operated at vacuum or pressure depending on process needs

Typical hardware for scrubbers

Sieve trays for fouling service (SS, Monel)
Metal random packings for many applications (SS, Monel)
Ceramic and carbon random packings for high temperature service
Plastic random packings for acid service (PP, GFPP, Noryl, PVDF, Teflon)
Metal structured packings for high efficiency/capacity (SS, Monel, Aluminum)
Tower internals in appropriate materials including distributors, supports and demisters

SAMPLE CALCULATION FOR AN ACID GAS ABSORBER

The first step in sizing a scrubber is to determine the column diameter. This is done based on recommended gas velocities. The second step is to determine the necessary liquid flow based on a recommended liquid loading and the column diameter. Once the liquid load and the column diameter are determined, the required packed bed depth will be determined. The variables that specify the packed bed depth are: Liquid and gas loads (mass velocities), Removal (concentrations in and out), Packing efficiency, and Type of system.

The calculation of the necessary design parameters vary with the type of application, the type of scrubbing liquid, the gas concentration levels, and the type of gas being scrubbed. **The information provided herein is for illustration purposes only and is intended only to provide guidance. Consult Jaeger Products, Inc. for a final and guaranteed design.**

DESIGN INFORMATION: *(generally supplied by the user)*
      Gas flow = 47 273 lb/h or 11 250 ACFM
      Contaminant = H_2S
      Concentration in = 200 ppm
      Concentration out = 0.1 ppm
      Temperature = 68 deg. F
      Pressure = 1 atm.

RECOMMENDATIONS: *(based on Jaeger's experience and data base)*
      Use NaOH solution as scrubbing liquid
      Design gas velocity = 300 ft/min (typical for H_2S scrubbers)
      Design liquid load = 3 gpm/ft^2 (typical)

CALCULATIONS:
      Column diameter = [(11 250 acfm/300 ft/min)/0.785]$^{1/2}$
            = 6.9 ft-----**Use 7 ft.**   *(calculated from gas flow and recommended gas velocity)*

      Liquid flow = 3 X 7^2 X 0.785 = **115 gpm** = 57 470 lb/h
          (calculated from column diameter and design liquid load)

      Gas mass velocity = 47 273 lb/h / 7^2 / 0.785 = 1229 lb/h/ft^2
          (calculated from gas flow and column diameter)

      Liquid mass velocity = 57 470 lb/h / 7^2 / 0.785 = 1494 lb/h/ft^2
          (calculated from liquid flow and column diameter)

      **Number of transfer units = NTU = ln (X_{in}/X_{out}) = ln (200 ppm/0.1 ppm) = 7.6
          (mass transfer term that depends on absorption factor and removal. Definition used here applies only to very dilute gases and absorption with very fast chemical reaction)

         ** Height of a transfer unit = HTU = 19.4" for equivalent loadings and 3 1/2 in. TRI-PACKS**(from mass transfer data table in Figure 3)
         (mass transfer term that depends on loadings and the characteristics of the packing)

         Packed bed height = NTU X HTU = 12.3 ft --------**Use 14 ft**
         (**Consult Jaeger for values for your application)

Vent

Mist eliminator

Liquid distributor

Caustic solution make-up

Caustic loop absorption.
Removal of: SO2, HCL,
H2S, Cl2, chlorine oxides,
HCN, HNO3, H2SO4, and other
acids

Packing

To disposal

Collector/support

Reciculating pump

Liquid distributor

Acid loop absorption.
Removal of NH3, soluble acids

Gas cooling and dust removal

Water

Packing

Support plate

Gas inlet

Recirculating pump

To waste water treatment

Figure 1. Typical two-stage gas absorption (scrubbing)
unit for NH₃ and acid gas removal.

Gas/Vapor Outlet

Mist Eliminator
(MEO1)

Manway

Reflux from
Condenser

Bed Limiter
(BL01)

Liquid Distributor
(LD03)

Random Packing
JAEGER TRI-PACKS®

Support Plate
(PS01)

Liquid Collector
Mixing Trough
(CR03)

Liquid Feed

Manway

Bed Limiter
(BL01)

Liquid Distributor
(LD04)

Jaeger Structured
Packing
(Max Pak™)

Support Grid
(PS02)

Liquid/Vapor
Feed

Manway

Flashing Feed Distributor
(LD08)

Structured Grid
Packing

Liquid Collector
with Draw Sump
(CROS)

Vapor Distributor
(GD03)

Reboiler Return or
Vapor Feed

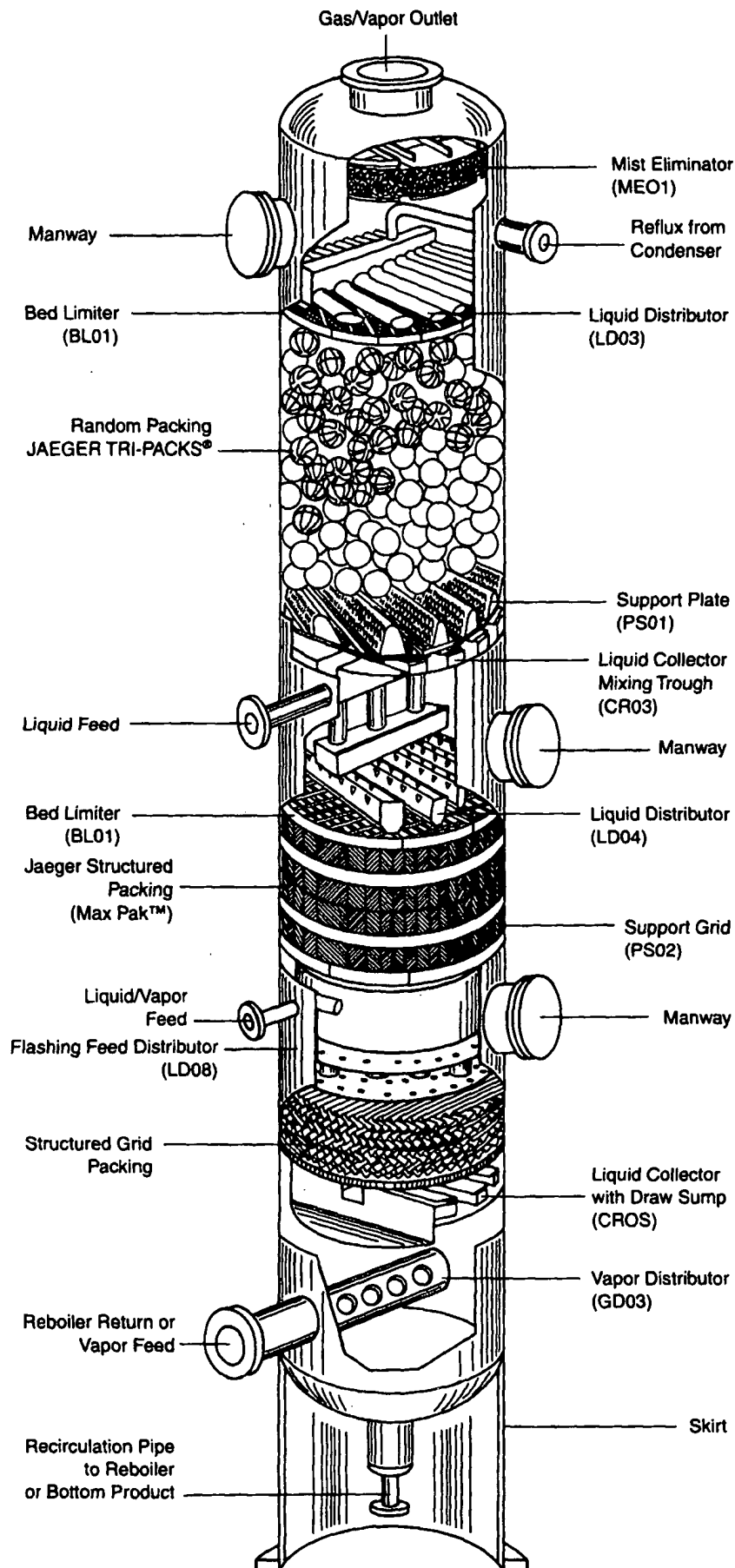Recirculation Pipe
to Reboiler
or Bottom Product

Skirt

Figure 2. Jaeger Products offers a complete line of
mass transfer devices for scrubbers.

PLASTIC JAEGER TRI-PACKS®

SPECIFICATIONS

Materials
Twelve standard, injection moldable plastics are available:

Polypropylene (PP)
Polyethylene (PE)
Polypropylene
  Glass-Filled (PPG)
Noryl® (PPO)
Polyvinylchloride (PVC)
Corzan™ (CPVC)

TopEx® (LCP)
Kynar® (PVDF)
Halar® (ECTFE)
Teflon® (PFA)
Tefzel® (ETFE)
Tefzel® Glass-
  Filled (ETFE-G)

Other plastics are available on request.

Properties Table

Size (in.)	1	1 1/4	2	3 1/2
Geometric Surface Area (ft²/ft³)	85	70	48	38
Packing Factor (1/ft)	28	25	16	12
Void Space (%)	90	92	93.5	95
Bulk Density (lb/ft³) (PP)	6.2	5.6	4.2	3.3

Sizes. Plastic Jaeger TriPacks® packings are made in four sizes:

1" Nominal
1 1/4" Nominal
2" Nominal
3 1/2" Nominal

IMPORTANT NOTE:
Design data presented in this bulletin are for preliminary calculations only. Contact Jaeger before finalizing calculations.

JAEGER TRI-PACKS® is a Registered Trademark of JAEGER PRODUCTS, INC.

MASS TRANSFER DATA

Absorption System	G (lb/hr-ft²)	L (lb/hr-ft²)	Temp (°F)	HTU-Inches		
				1	2	3 1/2
HCl-H₂O	1792	2048	77	7.0	10.6	12
HCl-NaOH	1567	2048	68	6.1	8.9	10
Cl₂-NaOH	1229	2202	122	9.9	14.5	16
NO₂-Na₂S₁N₂OH	717	1127	68	32.0	49.2	54
NH₃-H₂SO₄	492	1024	68	4.1	6.0	7
NH₃-H₂O	512	1024	68	5.6	8.4	10
NH₃-H₂O	512	4096	68	3.6	5.4	6.2
SO₂-NaOH	1946	4096	140	8.1	12.0	14
HF-H₂O	1844	3072	77	4.8	6.9	8.1
H₂S-NaOH	1229	1391	68	13.0	19.4	22

VOC Stripping	G (lb/hr-ft²)	L (lb/hr-ft²)	Temp (°F)	HTU-Inches		
				1	2	3 1/2
TCE(ppb)-H₂O	479	12264	77	21.5	28.9	31.1
TCE(ppm/ppb)-H₂O	600	12494	60	30.1	37.6	42.8
BTX(ppb)-H₂O	722	12264	70	31.4	33.8	33.0

Superior performance by design

JAEGER PRODUCTS, INC.

Figure 3. typical mass transfer performance data for scrubbing applications using Jaeger tri-Packs®

JAEGER PRODUCTS, INC.

HIGH PERFORMANCE TOWER PACKINGS AND COLUMN INTERNALS

1611 Peach Leaf
Houston, Texas 77039
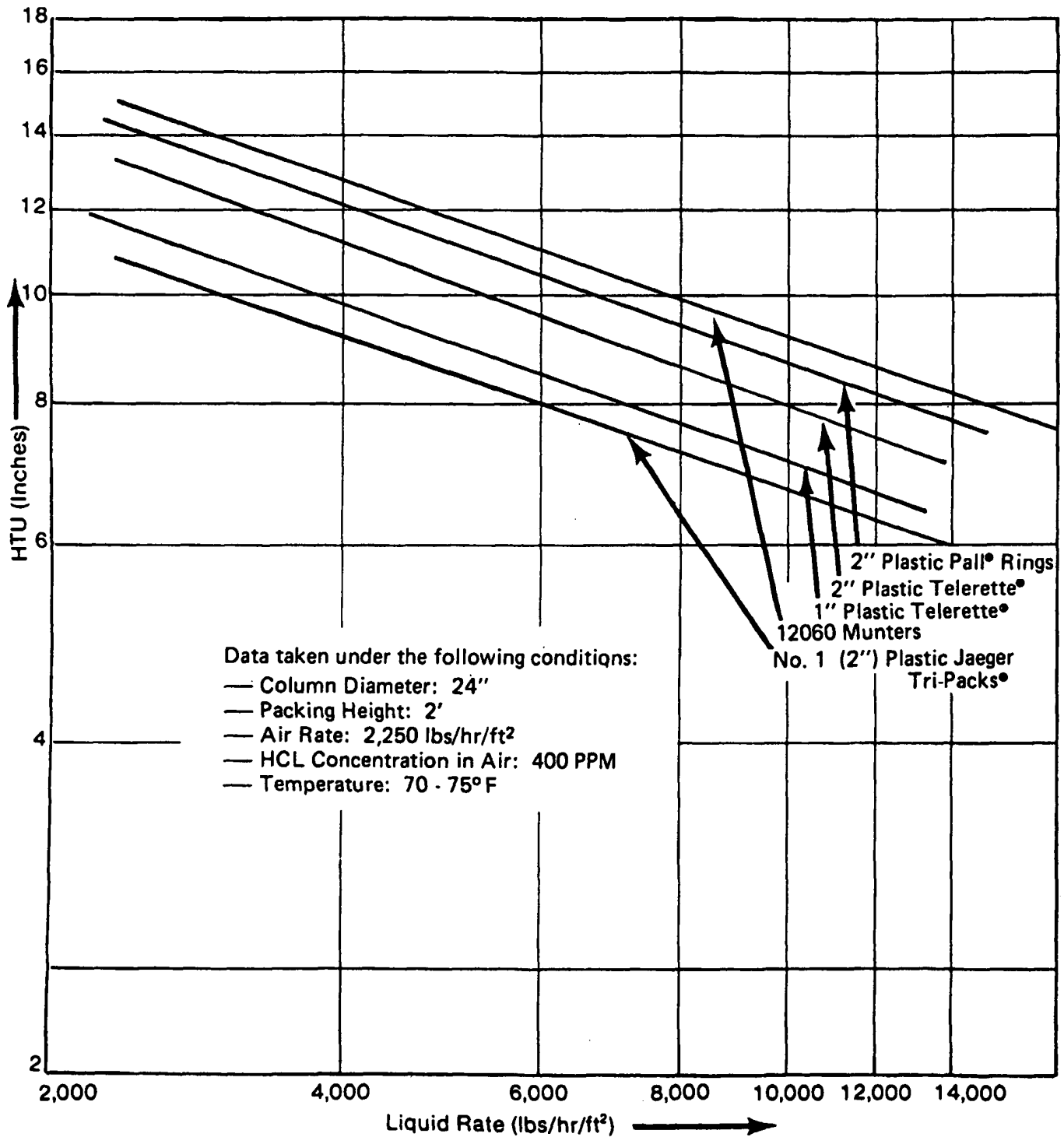
Phone: (281) 449-9500
FAX: (800) 678-0345

PRODUCT DATA PD-610

PLASTIC JAEGER TRI-PACKS®

Figure 4. Mass transfer efficiency.

HTU for HCL/H_2O Absorption

Jaeger Tri-Packs® shows better efficiency than
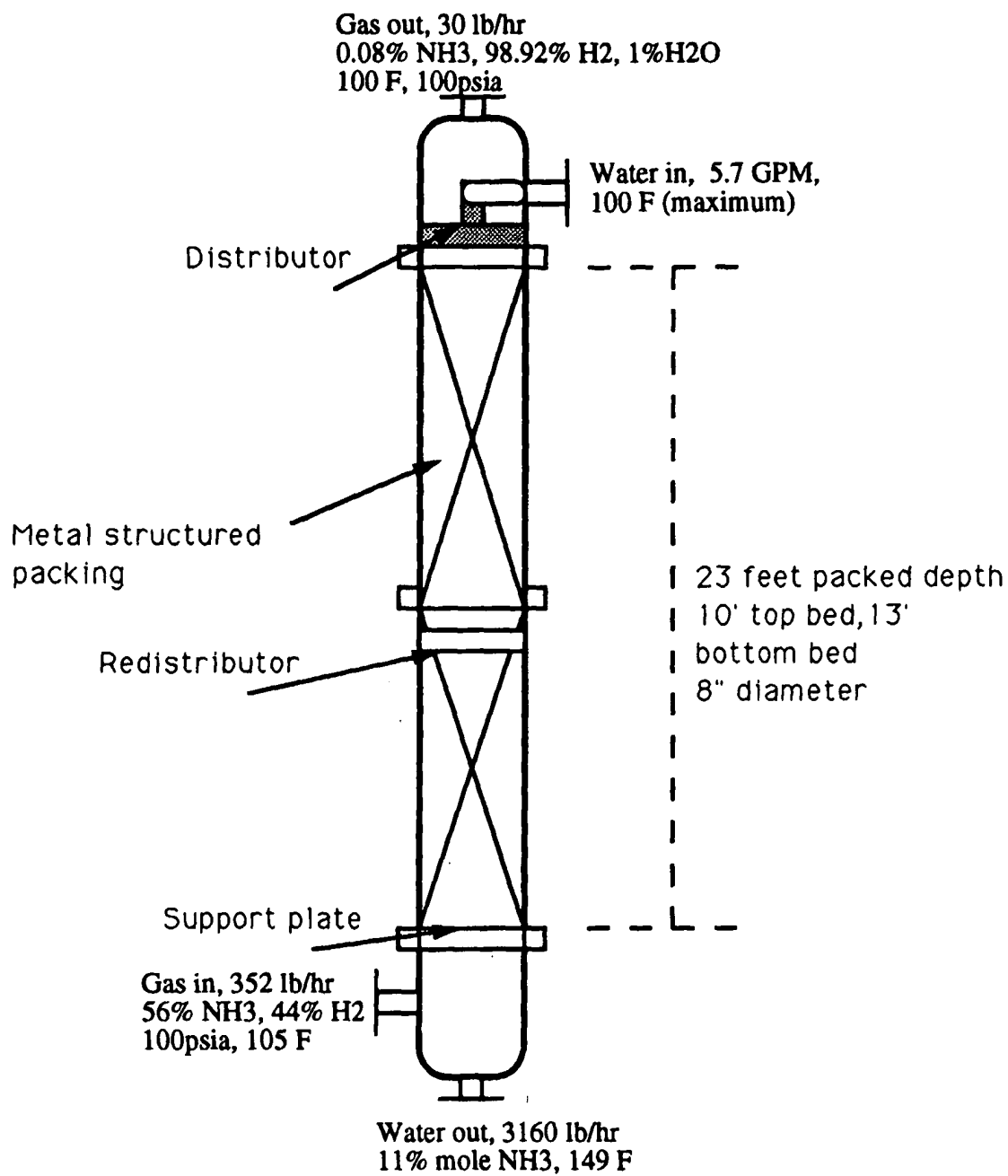other mass transfer devices.

Data taken under the following conditions:
— Column Diameter: 24"
— Packing Height: 2'
— Air Rate: 2,250 lbs/hr/ft²
— HCL Concentration in Air: 400 PPM
— Temperature: 70 - 75° F

2" Plastic Pall® Rings
2" Plastic Telerette®
1" Plastic Telerette®
12060 Munters
No. 1 (2") Plastic Jaeger
Tri-Packs®

Gas out, 30 lb/hr
0.08% NH3, 98.92% H2, 1%H2O
100 F, 100psia

Water in, 5.7 GPM,
100 F (maximum)

Distributor

Metal structured
packing

23 feet packed depth
10' top bed,13'
bottom bed
8" diameter

Redistributor

Support plate

Gas in, 352 lb/hr
56% NH3, 44% H2
100psia, 105 F

Water out, 3160 lb/hr
11% mole NH3, 149 F

Figure 5. Ammonia scrubber that uses a high efficiency
structured packing for minimum pressure drop.

ABSORPTION/SCRUBBING

Application information for design
(Copy, fill out and fax pertinent information and we will be glad to assist you with a design).

Company		
Person Responsible		
Address		
Telephone		Fax
Your Reference		Date

Description of problem, diagram:

Gas Phase

Flow rate: [   ]

Pressure: [   ]

Temperature: [   ]

Density: [   ]

	Components	Column Inlet concentration	Column Oulet concentration
1			
2			
3			
4			

Maximum pressure drop acceptable [   ] psi

Liquid Phase

Flow rate: [   ]

Temperature: [   ]

Density: [   ]

Composition: [   ] pH [   ]

Packing Material: [   ]

Column Material: [   ]

Accessories: [   ]

EXHIBIT C

Flue-Gas Desulfurization
("Scrubbers")

1. Introduction:

Scrubbers and absorbers are pieces of equipment installed in power plants to remove particulates and some selected gases from combustion fumes in order to meet emission standards. The usual gas being removed is SO_2, and we shall address the design of absorbing towers in this particular application.

The key aspect of the process is the dissolution of the gas from the fumes into a liquid made of water with suitable additives. The outflowing liquid is then collected, concentrated and landfilled or recycled.

Very similar equipment can be used to accomplish the opposite task, namely to "strip" a chemical out of a liquid solution by drawing (= evaporating) it into a gas passing across the solution.

2. General Description:

A scrubber is a tower in which gas and liquid flow against each other: the liquid solution flows downward while the gas bubbles to the top (Figure 1).
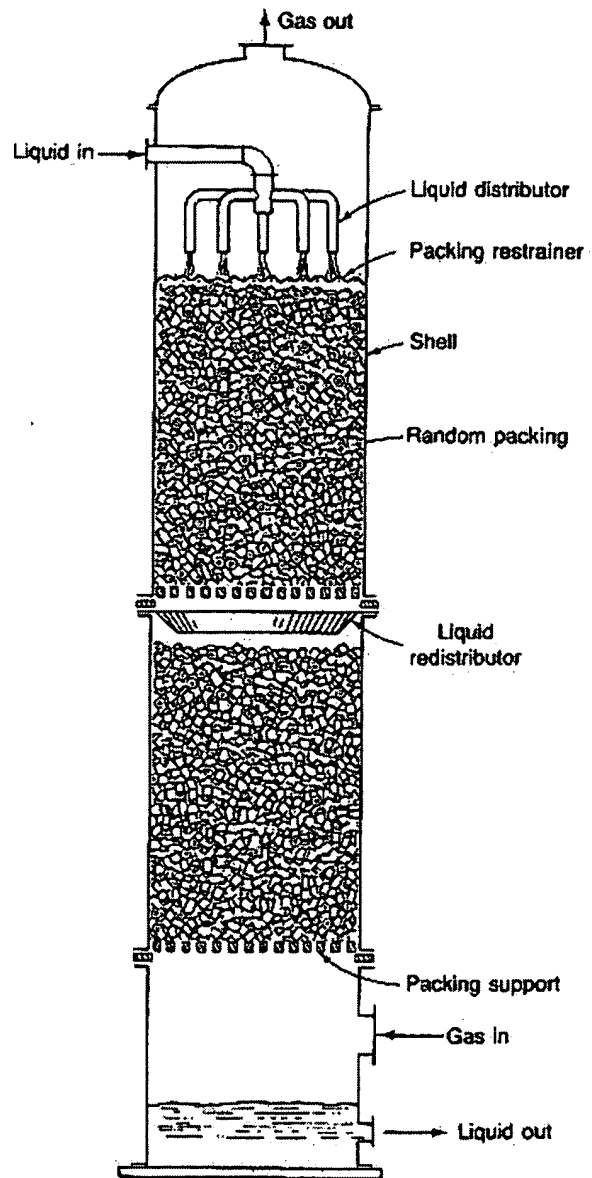
To maximize contact between liquid and gas, the tower is also packed with a large number of small objects forcing the liquid to percolate slowly through tortuous paths and the gas to rise up in small bubbles. As the liquid and gas compete for space, very intimate contact takes place between the two, and a very large area exists through which the transfer of properties can take place.

3. Chemical aspects:

The liquid used to "wash" the flue gas is a water-based calcium solution. Limestone ($CaCO_3$) is cheap and creates in water an alkaline environment:

$$CaCO_3 + H_2O \leftrightarrow Ca^{++} + HCO_3^- + OH^-$$
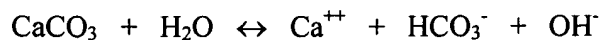
This alkalinity (presence of OH^- radicals) negates the acidity (presence of H^+ protons) formed by the SO_2 in solution:

Gas out

Liquid in

Liquid distributor

Packing restrainer

Shell

Random packing

Liquid redistributor

Packing support

Gas In

Liquid out

Figure 1. Cut-away sketch of a scrubber

2

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$$

The H^+ protons combine with the OH^- radicals to form water:

$$H^+ + OH^- \leftrightarrow H_2O$$

The radical HCO_3^- also binds with H^+ to create H_2CO_3 (carbonic acid), which creates an equilibrium with water (H_2O) and carbon dioxide (CO_2):

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \leftrightarrow H_2O + CO_2$$

The net result is the transformation of $CaCO_3$ to calcium ions (Ca^{++}) and the production of carbon dioxide and HSO_3^-:

$$CaCO_3 + 2\,SO_2 + H_2O \leftrightarrow Ca^{++} + CO_2 + 2\,HSO_3^-$$

The carbon dioxide bubbles up as a gas, while the HSO_3^- remains in the water solution (if the temperature is not too high - see final note below).

In the effluent hold tank, at the foot of the tower where the liquid is collected before final treatment, another load of limestone is added to the liquid, and a further reaction takes place:

$$CaCO_3 + 2\,HSO_3^- + Ca^{++} \rightarrow 2\,CaSO_3 + CO_2 + H_2O$$
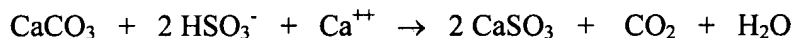
The $CaSO_3$ is a solid precipitate. It is important to have this precipitate occur in the effluent hold tank rather than in the tower itself. Otherwise, the tower would become clogged. To ensure proper functioning, it is therefore important to dose correctly the amount of limestone in the liquid fed at the top of the tower and to feed the remainder of the limestone to the effluent hold tank directly. The amount of limestone in the liquid is determined using stoichiometry (1 mole of $CaCO_3$ for 2 moles of SO_2, that is, 100 g of limestone per 128 g of sulfur dioxide removed from the flue gas) and is easily controlled by monitoring the pH, since it makes an alkaline solution.

The fact that some significant portion of the SO_2 in the liquid turns into another chemical, namely HSO_3^-, makes more room for SO_2 in the liquid and consequently promotes a greater suction of SO_2 from gas to liquid. When properly dosed, the limestone slurry is able to hold 6 to 15 times more S than pure water. This is very beneficial.

4. Physical Set-up and Primary Variables:

Figure 2 illustrates the physical set-up. The equipment mainly consists in a vertical tank, called tower, in which the fumes (vapor) are fed at the bottom, move upward through one or several layers of packed objects and exit at the top. Simultaneously, the cleaning liquid is poured from the top and trickles downward through the packed layers.
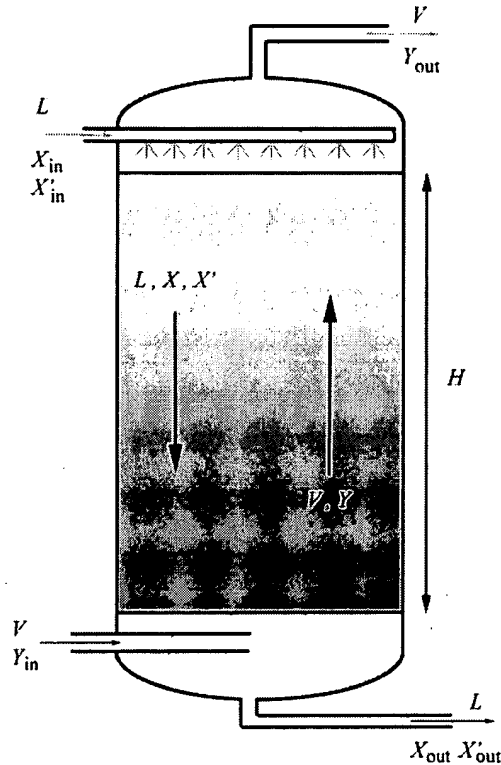

Figure 2. Sketch of mass fluxes and nomenclature

The complicated diversions of both fumes and liquid forced by the packed layers bring intimate contact between fumes and liquid, favoring the transfer of the gas to be removed from the former to the latter. The counter flow with vapor moving upward and liquid downward is very practical for two reasons: (1) It happens naturally by gravity as the liquid trickles down while the gas bubbles up through it, and (2) the fumes encounter increasingly less loaded liquid as they get progressively cleaner on their way upward.

We define variables as follows: X = number of moles of SO_2 in the liquid on a per-mass basis (moles per kg of liquid), X' = number of moles of HSO_3^- in the liquid on a per-mass basis (moles per kg of liquid), Y = number of moles of SO_2 in the vapor (fumes) on a per-mass basis (moles per kg of vapor), L = mass flow of liquid trickling down (kg of liquid per minute), V = mass flow of vapor bubbling upward (kg of vapor per minute), and H = height of the packed layers in the tower (meters).

4

The entrance and exit values are noted as: Y_{in} = inlet value of Y (at bottom), Y_{out} = exit value of Y (at the top), X_{in}, X_{in}' = inlet values of X and X' (at the top) and X_{out}, X_{out}' = exit values of X and X' (at the bottom). Since the vapor consists in the fumes coming from the combustion chamber, its chemical composition is known, and Y_{in} is therefore given. Regulatory standards impose a certain level of cleanliness in the fumes released to the environment and therefore set the value of Y_{out}. Alternatively, one may impose a certain efficiency of removal (ex. η = 95%), which sets the ratio Y_{out}/Y_{in} (= 1 − η).

To maximize the passage of SO_2 from vapor to liquid, we inject a clean liquid at the top and take $X_{in} = X_{in}' = 0$. Finally, X_{out} and X_{out}' can be whatever we wish them to be. If at all possible, however, we would want to maximize them in order to minimize the amount of liquid being used (minimization of energy for pumping to the top of the tower and minimization of volume to be treated downstream of the tower).

The removal of SO_2 from the vapor and its dissolution into the liquid make the mass flow of vapor (V) decrease upward and the mass flow of liquid (L) increase downward, but these changes are negligible because the absolute mass of SO_2 being transferred is rather modest; the fumes are mostly air and CO_2, and the slurry mostly water. We can then safely assume that the flow rates L and V stay at constant values throughout the tower.

5. Equilibria:

Inside the liquid, a chemical equilibrium exists between the two forms of sulfur, SO_2 and HSO_3^-. Assuming first-order chemical kinetics, we can then state that there exists a proportionality between the two concentrations, namely:

$$X' = cX$$

The coefficient c may be called the conversion factor. Its value ranges from 5 to about 14. Thus, the total amount of S in the solution is $X + X' = (1+c) X$, which is 6 to 15 times what the amount would have been without the calcium additive.

At the interface between gas and liquid, SO_2 is exchanged between the two until equilibrium is achieved. Equilibrium obeys Henry's Law of proportionality between gas and liquid phases:

$$Y = mX$$

At the temperature and pressure common in the operation of scrubbers, SO_2 equilibrium is achieved when the gas fraction is about 36 times the liquid fraction. Therefore, a practical value is m = 36. The value varies with the nature of the gas.

6. <u>Gas-Liquid Transfer:</u>

The actual flow in the tower is not at equilibrium and a one-way exchange takes place. It can be assumed that away from equilibrium, the transfer rate is proportional to the difference $Y - mX$, such that when $Y - mX$ is positive, there is an excess in the vapor phase and the transfer is from vapor to liquid (toward decreasing Y and increasing X), while when $Y - mX$ is negative, the transfer goes in the opposite direction. The transfer rate is furthermore proportional to the area of contact between gas and liquid. We model this as:

$$\text{transfer rate} = KA_c (Y - mX)$$

where K is a rate of transfer (mass per time and per area) and A_c is the area of contact.

On a graph in which Y is plotted against X (Figure 3), the equilibrium state is represented as a oblique straight line, dividing the X-Y plane into two regions. In the upper region, Y is bigger than mX and the transfer is from vapor to liquid, while in the lower region (below the line) Y is less than mX and the transfer is from liquid to gas. Since the objective is to transfer SO_2 from the gas to the liquid, we naturally want to remain on the upper side of the equilibrium line and the lower side is proscribed.
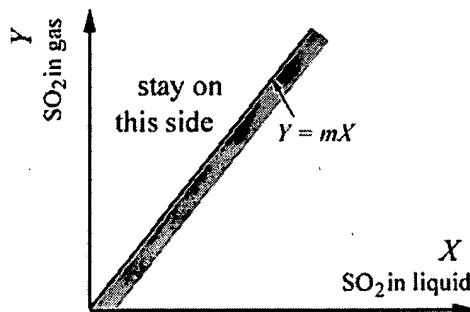

Figure 3. Equilibrium line on liquid-gas diagram

7. <u>Overall Mass Balance:</u>

An important relation is obtained when we perform a mass balance for a section of the tower, from an arbitrary level to the top (Figure 4).
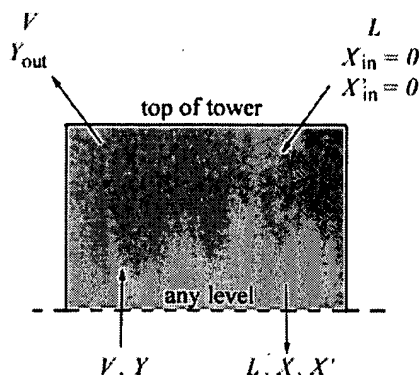
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Figure 4. Bulk mass-balance, from top of tower down to an arbitrary level

At the arbitrary level, the variables are Y, X and X', while at the top they are Y_{out}, X_{in} and X_{in}'. Since the amount of entering sulfur is equal to that going out during steady operation, the sum of the influxes, VY from below and $L(X_{in} + X_{in}')$ from the top, must be equal to the sum of the effluxes, VY_{out} from the top and $L(X + X')$ from below:

$$VY + L(X_{in} + X'_{in}) = VY_{out} + L(X + X')$$

Since $X_{in} = 0$ and $X' = cX$, a division by V yields:

$$Y = Y_{out} + (1+c)\frac{L}{V}X$$

On the X-Y plot, this relation corresponds to a straight line starting at $(X = 0, Y = Y_{out})$, corresponding to the top of the tower, and slanting upward with slope $(1+c)L/V$. This line is called the operating line. At the top of the graph, where Y reaches its maximum value Y_{in}, which corresponds to the bottom of the tower, one obtains the value of X_{out} (Figure 5).
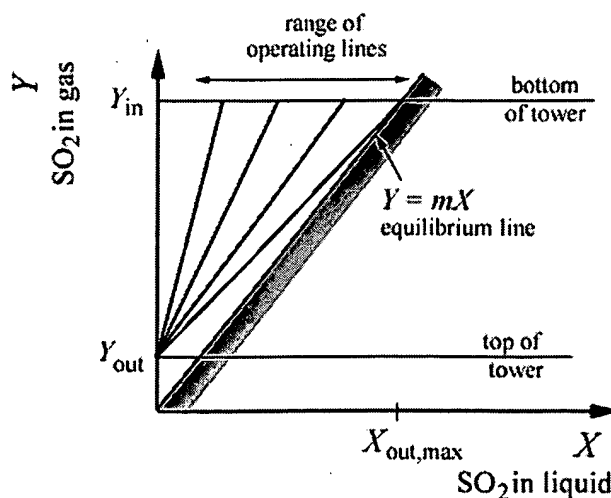

Figure 5. Operating line and its relation to the equilibrium line

Since the amount of liquid used (L) is free for the choosing, we can consider a series of different operating lines, one for every slope $(1+c)L/V$ considered. In order to stay on the upper side of the equilibrium curve, however, there exits a minimum acceptable slope, and there is therefore a minimum value of the liquid mass flow, L_{min}, that must be used. To this value corresponds the maximum possible value of X_{out}. These values are:

$$X_{out.max} = \frac{1}{m} Y_{in}$$

$$L_{min} = \frac{m}{1+c}\left(1 - \frac{Y_{out}}{Y_{in}}\right)V = \frac{m}{1+c}\eta V$$

In practice, for a reason that will be become clear later in the analysis, one must stay clear from the minimum value and adopt for L a value that is a multiple of the minimum, namely:

$$1.5 L_{min} \le L \le 3.0 L_{min}$$

8. Separate Mass Balances:

The operating line sets one relationship between the two variables, X and Y. A separate mass balance must be performed for each independently in other to determine X and Y as functions of position inside the tower. To do this, we now consider a thin slice of the packing inside the tower (Figure 6), from the level z to the level $z + dz$, counting z downward from the top ($z = 0$ where $Y = Y_{out}$ and $X = X_{in} = 0$).
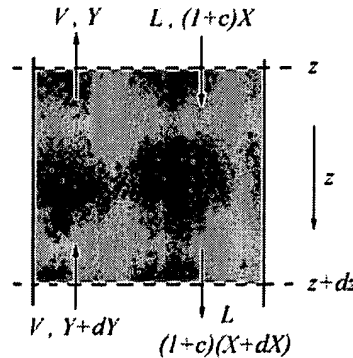

Figure 6. Local mass balance

The steady-state budgets express that the rate at which the amount in each phase (gas or liquid) enters the slice is equal to the rate at which it exits plus or minus the amount exchanged with the other phase:

$$V(Y + dY) = VY + KdA_c(Y - mX)$$

$$(1 + c)LX = (1 + c)L(X + dX) - KdA_c(Y - mX)$$

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where dA_c is the contact surface area between liquid and gas inside the slice under consideration. If we define a as the surface area made available by the packed objects per volume of packing (in ft^2 per ft^3- see Figure 7), then dA_c is equal to a times the volume of the slice. If A is the cross-section area of the tower, this volume is Adz, and the contact area in that volume is $dA_c = aAdz$. The previous budget equations become:

$$V\, dY = +K\, aA\, (Y - mX)\, dz$$

$$(1+c)L\, dX = +K\, a\, A\, (Y - mX)\, dz$$

Or, in the form of differential equations:

$$\frac{dY}{dz} = \frac{KaA}{V}(Y - mX) \qquad \frac{dX}{dz} = \frac{KaA}{(1+c)L}(Y - mX).$$

Since the operating line sets a relationship between Y and X, we can replace Y in terms of X in the second equation to obtain a single equation for the variable X:

$$\frac{dX}{dz} = \frac{KaA}{(1+c)L}Y_{out} + \frac{KaA[(1+c)L - mV]}{(1+c)LV}X$$

Integration from the top (where $X = 0$ at $z = 0$) downward ($z > 0$) yields:

$$X(z) = \frac{V(e^{\lambda z} - 1)}{(1+c)L - mV}Y_{out}$$

where the coefficient λ in the exponent is defined by

$$\lambda = \frac{KaA[(1+c)L - mV]}{(1+c)LV}$$

The accompanying solution for Y is:

$$Y(z) = \frac{(1+c)Le^{\lambda z} - mV}{(1+c)L - mV}Y_{out}$$
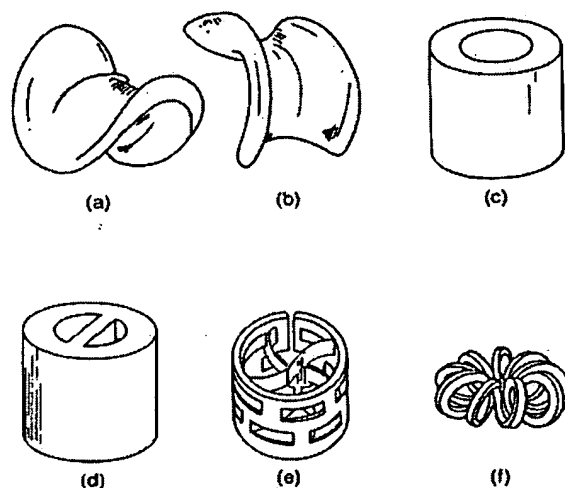
Table 13.4   Tower Packing Characteristics

Type	Material	Nominal Size, in.	Bulk Density,† lb_m/ft^3	α Total Area,† ft^2/ft^3	Porosity ϵ	Packing Factors‡ F_p	f_p
Berl saddles	Ceramic	½	54	142	0.62	240	§1.58
		1	45	76	0.68	110	§1.36
		1½	40	46	0.71	65	§1.07
Intalox saddles	Ceramic	½	46	190	0.71	200	2.27
		1	42	78	0.73	92	1.54
		1½	39	59	0.76	52	1.18
		2	38	36	0.76	40	1.0
		3	36	28	0.79	22	0.64
Raschig rings	Ceramic	½	55	112	0.64	580	§1.52
		1	42	58	0.74	155	§1.36
		1½	43	37	0.73	95	1.0
		2	41	28	0.74	65	§0.92
Pall rings	Steel	1	30	63	0.94	48	1.54
		1½	24	39	0.95	28	1.36
		2	22	31	0.96	20	1.09
	Polypropylene	1	5.5	63	0.90	52	1.36
		1½	4.8	39	0.91	40	1.18

† Bulk density and total area are given per unit volume of column.
‡ Factor F_p is a pressure-drop factor and f_p a relative mass-transfer coefficient.
§ Based on NH_3–H_2O data; other factors based on CO_2–$NaOH$ data.

SOURCE: McCabe, W. L., Smith, J. C., and Harriott, D., *Unit Operations of Chemical Engineering*,
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Figure 7. Typical tower packing material and corresponding properties

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From this, we can determine the values at the bottom. If H is the height of the packed

layer inside the tower where the gas-to-liquid exchange takes place, the bottom values are obtained for $z = H$:

$$X_{out} = \frac{V(e^{\lambda H} - 1)}{(1+c)L - mV} Y_{out}$$

Since the Y_{in} value is known, the last equation sets a constraint on the dimensions of the tower.

$$Y_{in} = \frac{(1+c)Le^{\lambda H} - mV}{(1+c)L - mV} Y_{out}$$

9. Absorption-Tower Design:

When designing a scrubber, the performance is set, that is, one knows the composition of both entering gas (Y_{in}) and exiting gas (Y_{out}). Therefore, the percentage of removal expressed as $\eta = 1 - Y_{out}/Y_{in}$ (usually on the order of 95%) is also known. The preceding equation, linking the entrance and exit values of Y, should then be solved for H, and we successively write:

$$\frac{e^{\lambda H} - mV/(1+c)L}{1 - mV/(1+c)L} = \frac{Y_{in}}{Y_{out}} \quad \Rightarrow \quad \frac{e^{\lambda H} - \beta}{1 - \beta} = \frac{1}{1 - \eta}$$

$$\Rightarrow \quad e^{\lambda H} = \frac{1 - \beta}{1 - \eta} + \beta \quad \Rightarrow \quad \lambda H = \ln\left(\frac{1 - \beta}{1 - \eta} + \beta\right)$$

where the variable β is defined for convenience as the dimensionless ratio

$$\beta = \frac{mV}{(1+c)L}$$

Solving for the height H of packing inside the tower and expressing the parameter λ in terms of original variables, we obtain:

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$$H = \frac{V}{KaA} \frac{\ln\left(\frac{1-\beta}{1-\eta} + \beta\right)}{1-\beta}$$

This expression can be thought of as the product of a unit height, called the height of a transfer unit (HTU)

$$HTU = \frac{V}{KaA}$$

with a dimensionless number N:

$$N = \frac{\ln\left(\frac{1-\beta}{1-\eta} + \beta\right)}{1-\beta}$$

In this manner, the height of the packing in the tower appears to be N times an HTU.

10. Height of a transfer unit (HTU):

The HTU has a physical significance. Indeed, consider a slice of finite thickness Δz, from z-Δz to z, as depicted in Figure 8.
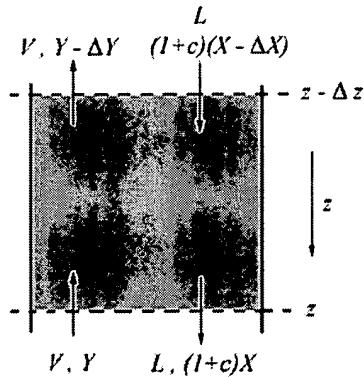

Figure 8. Mass balance for a slice of finite thickness

Now assume that this layer is well mixed and has a thickness sufficient to create chemical equilibrium among the outgoing flows, namely the vapor concentration Y-ΔY exiting from the top is in equilibrium with the liquid concentration X exiting from the bottom:

$$Y - \Delta Y = mX$$

which yields

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$$\Delta Y = Y - mX$$

At the same time, the overall SO_2 budget (all that goes out is accounting for all that goes in) imposes

$$V(Y - \Delta Y) + L(1+c)X = VY + L(1+c)(X - \Delta X)$$
$$\Rightarrow \quad V\Delta Y = L(1+c)\Delta X$$

If we now discretize the continuous equations (by approximating the derivatives with respect to z as finite differences over the Δz interval), we have:

$$\frac{\Delta Y}{\Delta z} = \frac{KaA}{V}(Y - mX) \qquad \frac{\Delta X}{\Delta z} = \frac{KaA}{(1+c)L}(Y - mX)$$

With the preceding expressions for the differences ΔX and ΔY, both these relations reduce to:

$$\frac{1}{\Delta z} = \frac{KaA}{V}$$

In other words, $\Delta z = HTU$ and a transfer unit can be conceived as a slice of the tower over which local equilibrium can be reached.

The number N of such units can be derived graphically (Figure 9) by constructing a staircase between the operating line and the equilibrium line such that every step corresponds to $Y - \Delta Y = mX$, and then counting the number of steps.
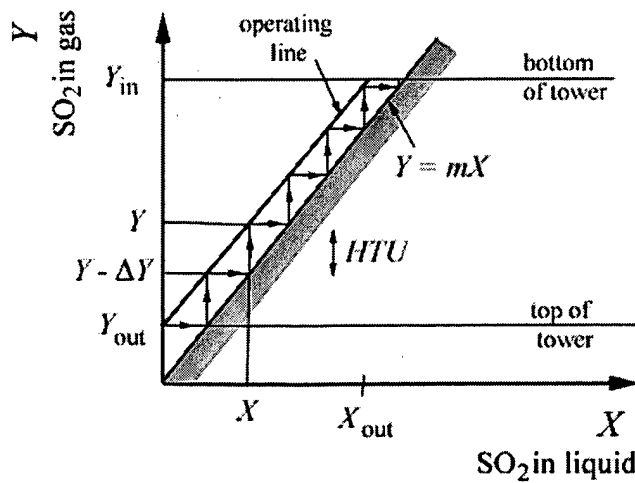

Figure 9. Graphical staircase construction to determine the number of transfer units

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In the expression for *HTU*, the vapor mass flow *V* and the tower's cross-sectional area *A* can be combined to introduce the gas velocity *v* (defined from $V = \rho_v A v$, where ρ_v is the gas density). This yields:

$$HTU = \frac{\rho_v v}{Ka}$$

Because a greater gas velocity promotes better contact, the density of contact area *a* is somewhat dependent on the gas velocity *v*, and it is often impractical to try to estimate *HTU* from its separate ingredients. In many applications, therefore, the value of *HTU* is often determined experimentally. Note that, in any event, the value of *HTU* does not depend on the overall dimensions of the tower and absolute flow rates, but only on local variables, such as *K*, *a* and *v*.

At this point, we can also appreciate why the liquid flow rate *L* may not be taken at its minimum value L_{min}. If it were ($L = L_{min}$), the number of steps would be infinite and the required tower height would be infinity! ($N \to \infty$ as $\beta \to \beta_{max} = mV/(1+c)L_{min} = 1/\eta$). This is why the actual liquid flow rate needs to be a multiple of the minimum value.

11. Flooding:

To reduce the diameter of the tower and therefore the cost, one wishes to pass the required liquid and gas flows through the narrowest possible section, that is, at the highest possible speeds. There is, however, a limit on the gas velocity. If the gas velocity exceeds a certain threshold, it literally blows the liquid away from the packing material and prevents it from trickling downward. The result is an accumulation of liquid above the packed layers and flooding in the upper section of the tower. To determine the safest possible gas speed, the procedure is to calculate the flooding speed and then take a fraction of the latter.

Figure 13.6   Generalized correlation for flooding and pressure drop in packed towers.
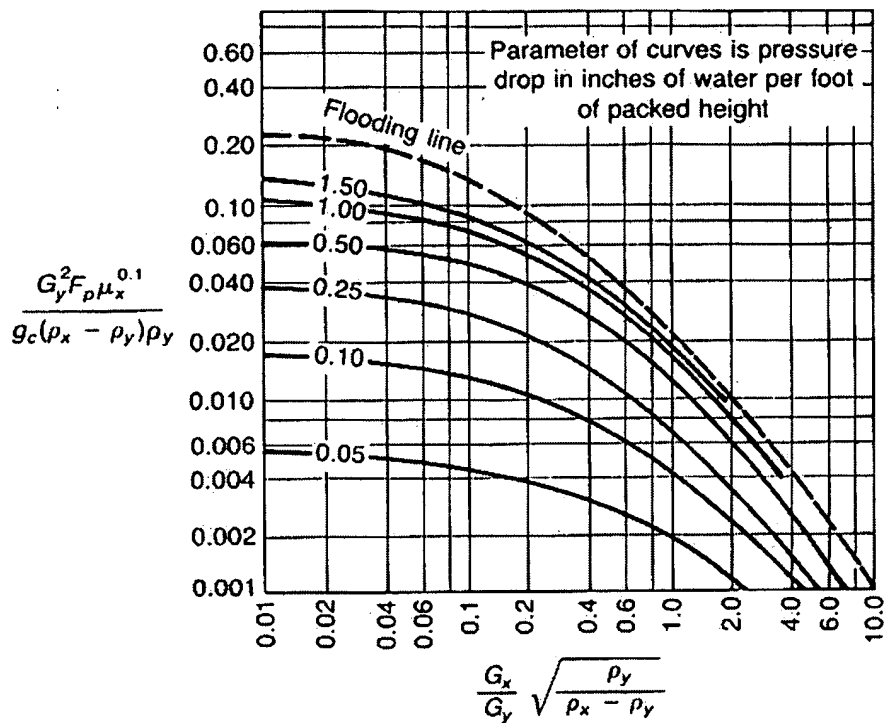
The flooding velocity is estimated using Figure 13.6, which is a logarithmic plot of

$$\frac{G_y^2 F_p (\mu_x)^{0.1}}{g_c(\rho_x - \rho_y)\rho_y} \quad \text{versus} \quad \frac{G_x}{G_y}\sqrt{\frac{\rho_y}{\rho_x - \rho_y}}$$

where

F_p = packing factor from Table 13.4, ft^{-1} (see page 403)

ρ_x = liquid density, lb_m/ft^3

ρ_y = gas density, lb_m/ft^3

μ_x = liquid viscosity, cp $= 0.80$ cp

g_c = proportionality constant, 32.17 $\text{ft-lb}_m/\text{s}^2\text{-lb}_f$

$L/A = G_x$ = liquid mass flux, $\text{lb}_m/\text{s-ft}^2$

$V/A = G_y$ = gas mass flux, $\text{lb}_m/\text{s-ft}^2$

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The flooding speed is determined from the top curve on the accompanying graph (labeled Figure 13.6). The abscissa is first calculated using the already known gas and liquid mass fluxes (noting that G_x/G_y is equal to L/V) and the densities of both liquid (ρ_x) and gas (ρ_y). From the abscissa, one goes up the graph to the top, dashed curve - labeled "Flooding line" - and across to determine the corresponding ordinate. In the expression forming the ordinate, all factors should be known except the gas mass flux G_y. Thus, reading the graph provides a value for G_y. The flooding gas velocity can then be obtained by eliminating mass with the density: $v_{flooding} = G_y/\rho_y$. The recommended operational speed is half of the flooding speed, thus:

$$v = 0.5 v_{flooding} = 0.5 \frac{G_y}{\rho_y}$$

Once the gas speed is set, the cross-sectional area A of the tower is determined in order to have the correct total gas flow rate (using $V = \rho_y v A$), and the required inner diameter of the tower d is calculated (using $A = \pi d^2/4$). Thus,

$$d = \sqrt{\frac{4V}{\pi \rho_y v}}$$

12. Final Note:

The fumes exiting the furnace are hot and need to be cooled significantly before entering the scrubber. This is necessary to reduce the volatility of HSO_3^- (into which SO_2 turns once in the liquid phase) and therefore to promote its retention into the liquid used for the scrubbing. Reheating the cleaned fumes is necessary afterwards for more efficient release through the smokestack to the atmosphere.

13. Recapitulation of design procedure:

- Establish the expected performance $P = 1 - Y_{out}/Y_{in}$.

- From Y_{in}, Y_{out} and the equilibrium line, determine L_{min}, paying attention to the factor $(1+c)$ in order to take into account the chemical changes of SO_2.

- From L_{min}, set the L value using the rule $1.5\ L_{min} \leq L \leq 3.0\ L_{min}$.

- Determine the value of the parameter $\beta = 36V/(1+c)L$.

- Calculate the number N of stages, using its expression in terms of P and β.

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- Select or estimate a value for the height of a transfer unit (*HTU*).

- Determine the tower height $H = N\,HTU$.

- Determine the flooding gas mass flux G_y from the flooding curve (Fig. 13.6).

- Set the gas velocity at half flooding value: $v = 0.5\,G_y/\rho_y$.

- Determine the tower cross-sectional area A and then its diameter d.

- Estimate the amount of limestone needed.

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